

# Interplay of frustration, magnetism, charge ordering, and covalency in the ionic Hubbard model on the triangular lattice at three-quarters filling

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We investigate the ionic Hubbard model on a triangular lattice at three-quarters filling. This model displays a subtle interplay between metallic and insulating phases and between charge and magnetic order. We find crossovers between Mott, charge transfer and covalent insulators and magnetic order with large moments that persist even when the charge transfer is weak. We discuss our findings in the context of recent experiments on the layered cobaltates  $A_{0.5}CoO_2$  ( $A=K, Na$ ).

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The competition between metallic and insulating states in strongly correlated materials leads to many novel behaviours. The Mott insulator occurs when a single band is half-filled and the on-site Coulomb repulsion,  $U$ , is much larger than hopping integral,  $t$ . A menagerie of strongly correlated states is found when a system is driven away from the Mott insulating state, either by doping, as in the cuprates [1], or reducing  $U/t$ , as in the organics [2]. Geometric frustration causes yet more novel physics in Mott systems [2]. Therefore the observation of strongly correlated phases in the triangular lattice compounds  $A_{0.5}CoO_2$ , where  $A$  is K or Na [3], has created intense interest.

An important model for investigating insulating states in correlated materials is the ionic Hubbard model. On a half-filled square lattice this model displays a crossover between Mott and band insulating states which has been analyzed with quantum Monte Carlo (QMC) [4], dynamical mean field theory (DMFT) and its cluster extensions [5]. However, except for the case of one dimension [6], this model has not been studied away from half-filling [7] and/or on geometrically frustrated lattices.

In this Letter we study the ionic Hubbard model on a triangular lattice at three-quarter filling. This Hamiltonian displays a subtle interplay between metallic and insulating phases and charge and magnetic order. It has regimes analogous to Mott, charge transfer [8], and covalent insulators [9]. The study of this model is motivated in part by our recent proposal [10] that it is an effective low-energy Hamiltonian for  $Na_xCoO_2$ , at values of  $x$  at which ordering of the sodium ions occurs.

The Hamiltonian for the ionic Hubbard model is

$$H = -t \sum_{\langle ij \rangle \sigma} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{i\sigma} \epsilon_i n_{i\sigma}, \quad (1)$$

where  $c_{i\sigma}^\dagger$  annihilates (creates an electron with spin  $\sigma$  at site  $i$ ,  $t$  is the hopping integral,  $U$  is the effective Coulomb repulsion between electrons on the same site, and  $\epsilon_i$  is

a the site energy. We specialise to the case with two sublattices, A ( $\epsilon_i = \Delta/2$ ) and B ( $\epsilon_i = -\Delta/2$ ), consisting of alternating rows, with different site energies on the two sublattices (c.f., Fig. 15 of Ref. 10). This is the lattice relevant to  $A_{0.5}CoO_2$  where the difference in site energies results from the ordering of the A-atoms [11, 12, 13].

Two limits of model (1) at 3/4-filling may be easily understood. For non-interacting electrons,  $U = 0$ , a metallic state occurs for all  $\Delta$  as at least one-band crosses the Fermi energy. In the atomic limit  $t = 0$ , and  $U > \Delta$  one expects a charge transfer insulator with a charge gap of about  $\Delta$  whereas for  $U < \Delta$  a Mott insulator with charge gap of  $U$  occurs. However, realistic parametrization of  $A_xCoO_2$  materials imply  $U \gg \Delta$  and  $\Delta \sim |t|$  [14]; we will show below that in this parameter regime the model show very different behaviour from either of the limits discussed above. This interesting regime needs to be analyzed using non-perturbative and/or numerical techniques. Thus, we have performed Lanczos diagonalization calculations on 18 site clusters with periodic boundary conditions.

In Fig. 1 we plot the charge transfer,  $n_B - n_A$  as a function of  $\Delta/|t|$  for several values of  $U$ . We also plot  $n_B - n_A$  in two analytically tractable limits: the non-interacting limit,  $U = 0$  [15]; and the strong coupling limit  $U \gg \Delta \gg |t|$  [16]. Several interesting effects can be observed in this calculation. Firstly, the sign of  $t$  strongly effects the degree of charge transfer on the triangular lattice. Secondly, charge transfer depends only weakly on  $U$ . Thirdly, regardless of the sign of  $t$  or the magnitude of  $U$ , the charge transfer increases rather slowly as  $\Delta$  increases.

The charge gap, i.e., the difference in the chemical potentials for electrons and holes, is  $\Delta_c \equiv E_0(N+1) + E_0(N-1) - 2E_0(N)$ , where  $E_0(N)$  is the ground state energy for  $N$  electrons. We plot the variation of  $\Delta_c$  with  $\Delta$  for various values of  $U$  in Fig. 2.  $\Delta_c$  vanishes for  $U = 0$ , however finite size effects mean that we cannot accurately calculate  $\Delta_c$  for small  $\Delta$ .  $\Delta_c = \Delta$  for  $t = 0$

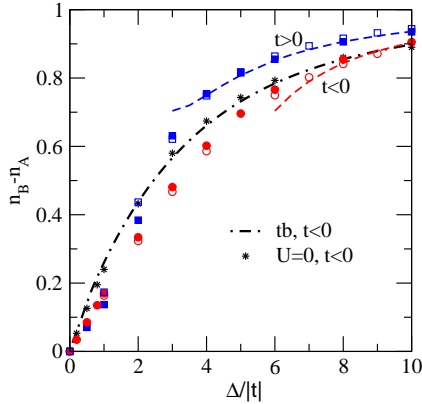


FIG. 1: (Color online) Variation of the charge transfer with  $\Delta$  for different Coulomb repulsion energies. Lanczos results on an 18-site cluster for:  $U/|t| = 0$  (stars), 15 (open symbols) and 100 (filled symbols) are shown. The  $U = 0$  results are in excellent agreement with the infinite lattice tight-binding (tb) result (dashed-dotted line) [15]. Strong coupling results (dashed lines) are also shown for comparison.

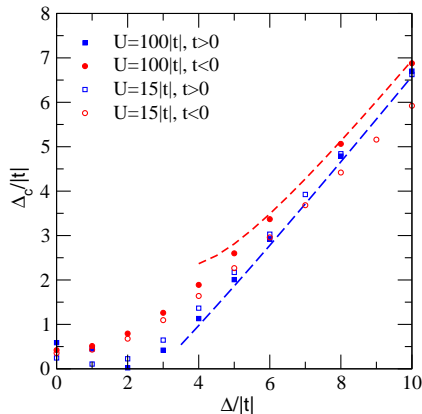


FIG. 2: (Color online) Variation of the charge gap,  $\Delta_c$ , with  $\Delta$  for  $U/|t| = 15$  and 100 (the charge gap is zero for  $U = 0$ ). The tendency towards an insulating state is greater for  $t < 0$  than for  $t > 0$ . Dashed lines show the strong coupling limit:  $U \gg \Delta \gg t$ . Note that although strong correlations are essential for creation of the charge gap they are not required for the charge transfer, c.f., Fig. 1. Note that, for  $U \gg \Delta$  with  $U$  large, the charge gap is robust against the value of  $U$ .

and  $U \gg \Delta$ ; this result is reminiscent of a charge transfer insulator [8]. Both perturbative [17] and numerical results show that the charge gap depends on the sign of  $t$  due to the different magnetic and electronic properties arising from the geometrical frustration of the triangular lattice. In contrast, on a square lattice,  $\Delta_c$ , does not depend on the sign of  $t$ .

In the limit,  $\Delta \gg U \gg |t|$ , the A and B sublattices are well separated in energy; the B sites are doubly occupied (i.e., the B-sublattice is a band insulator) and the A sub-

lattice is half-filled and hence becomes a Mott insulator. If there were no hybridisation between that chains, one would find a metallic state for any finite charge transfer from the B-sites to the A-sites (self doping), even for  $U \gg |t|$  as the A-chains are now electron-doped Mott insulators and the B-chains are hole-doped band insulators. However, Fig. 2 shows that the insulating regime of the model extends far beyond the well understood  $n_B - n_A = 1$  regime. This is because the real space interpretation is incorrect as hybridization between A and B chains is substantial. For  $|t| \sim \Delta \ll U$  the system can remain insulating with a small gap  $[O(t)]$ . This state is analogous to a covalent insulator [9].

One expects that for  $\Delta = 0$  the ground state is metallic as there the system is  $3/4$ -filled. However, a small but finite  $\Delta = 0^+$  leads to a strongly nested Fermi surface for  $t > 0$  whereas for  $t < 0$  the Fermi surface rather featureless. Thus, rather different behaviors might be expected for different signs of  $t$  even at weak coupling. At large  $U$  our exact diagonalization results suggest that a gap may be present even for a small value of  $\Delta/t$ . However finite-size effects, inherent to the method, mean that it is not possible to resolve whether a gap opens at  $\Delta = 0$  or at some finite value of  $\Delta$ .

To test this covalent insulator interpretation in the  $\Delta \sim |t|$  and large  $U$  regime we have also calculated the spectral density,  $A(\omega)$ , c.f., Fig. 3. There are three distinct contributions to the  $A(\omega)$ : at low energies there is a lower Hubbard band; just below the chemical potential ( $\omega = \mu$ ) is a weakly correlated band; and just above  $\omega = \mu$  is the upper Hubbard band. Furthermore, the large energy separation, much larger than the expected  $U = 15|t|$ , between the lower and upper Hubbard bands is due to an upward (downward) shift of the upper (lower) Hubbard bands due to the strong hybridization. In contrast, in the strong coupling limit  $A(\omega)$  has a much larger gap,  $O(\Delta)$ , between the contributions from the weakly correlated band and the upper Hubbard band.

The magnetic moment associated with the possible antiferromagnetism,  $m_\nu = (3\langle S_i^z S_j^z \rangle)^{1/2}$ , where  $\nu = A$  or  $B$  and  $S_i^z = \frac{1}{2}(n_{i\uparrow} - n_{i\downarrow})$ , is evaluated between two next-nearest neighbors on the  $\nu$  sublattice at the center of cluster (to reduce finite size effects [18]). Fig. 4 shows that  $m_A$  increases with  $\Delta$  and is substantially enhanced by  $U$ , whereas  $m_B$  is always small. This is in marked contrast to a spin density wave, as predicted by Hartree-Fock calculations where the magnetic moment is far smaller than that experimentally observed [19].

We now turn to discuss the consequences of our results for understanding experiments; for simplicity and concreteness we focus on  $\text{Na}_x\text{CoO}_2$ . The  $x = 0.5$  materials have remarkably different properties from those on other values of  $x$  [20, 21]. Above 51 K the intralayer resistivity of  $\text{Na}_{0.5}\text{CoO}_2$  is weakly temperature dependent with values of a few  $\text{m}\Omega\text{cm}$  [20] characteristic of a bad metal [10]. Below 51 K the resistivity increases, consis-

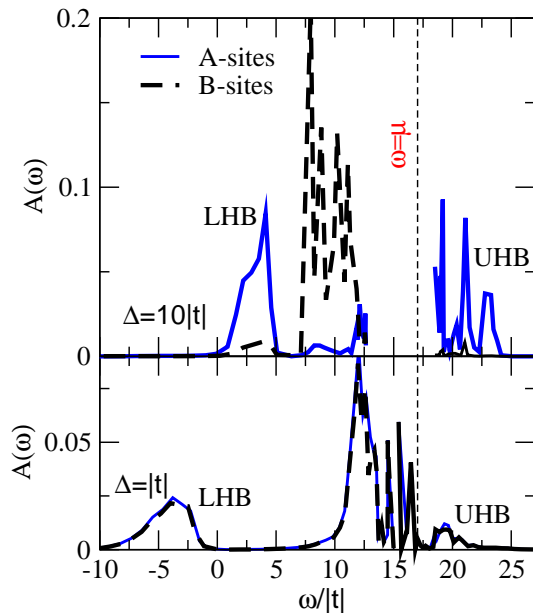


FIG. 3: (Color online) Evolution from a charge transfer insulator to a covalent insulator. The energy dependence of the spectral density,  $A(\omega)$ , is shown for two different parameter regimes of the model with  $t < 0$  and  $U = 15|t|$ . The spectral density in the upper panel ( $\Delta = 10|t|$ ) is that characteristic of a charge transfer insulator [9] there is a single weakly correlated band largely associated with the B sites and lying between lower (LHB) and upper (UHB) Hubbard bands (separated by  $\sim U$ ) that are largely associated with the A sites and  $\Delta_c \sim \Delta$ . In contrast, the lower panel ( $\Delta = |t|$ ) shows a spectral density characteristic of a covalent insulator [9]: there are only small difference between A and B sites, the separation of the LHB and UHB is  $> U$ , and  $\Delta_c \sim |t|$ .

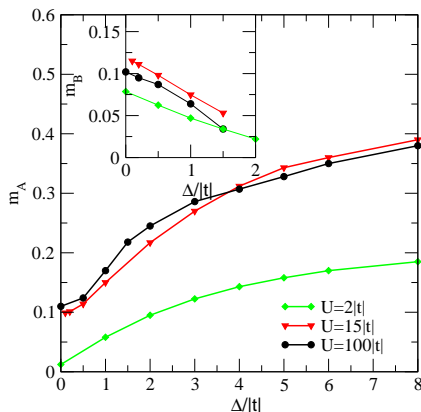


FIG. 4: (Color online) The magnetic moment as a function of  $\Delta$  for  $t < 0$  and various  $U$ . The magnetic moment on the A sites,  $m_A$ , (main panel) is strongly enhanced when  $U \gg |t|$ . The inset shows the moment on the B sublattice.  $m_B$  is much smaller, reduced by  $\Delta$ , and only weakly dependent on  $U$ . These results demonstrate that, for large  $U$  and  $\Delta \gtrsim |t|$ , the electrons on the A-sublattice are much more strongly correlated than those on the B-sublattice despite the small charge transfer (see Fig. 1).

tent with a small gap opening ( $\sim 10$  meV) [20]. Thus a (bad) metal-insulator transition occurs at 51 K. The insulating state of  $\text{Na}_{0.5}\text{CoO}_2$  has a number of counter-intuitive properties, not the least of which is the absence of strong charge ordering. NMR observes no charge ordering up to a resolution of  $n_B - n_A < 0.4$  [22, 23], while neutron crystallography suggest  $n_B - n_A \simeq 0.12$  [11]. Thus the insulating state is not the simple charge-transfer-like state predicted by (1) in the strong coupling limit.  $\text{Na}_{0.5}\text{CoO}_2$  develops a commensurate magnetic order below 88 K [22, 24]. A large magnetic moment [ $m = 0.26(2)\mu_B$  per magnetic Co ion] is observed in spite of the weak charge order [note that classically  $m < (n_B - n_A)\mu_B/2$ ]. Above 100 K the optical conductivity [21] shows no evidence of a Drude peak, consistent with a bad metal. In the insulating phase spectral weight is lost below  $\sim 10$  meV, consistent with the gap seen in the dc conductivity and a peak emerges at  $\sim 20$  meV, which is too sharp and too low energy to correspond to a Hubbard band [21]. ARPES shows that the highest energy occupied states are  $\sim 10$  meV below the Fermi energy [25]. No equivalent insulating state is seen in the misfit cobaltates [22], which supports the contention that Na-ordering is vital for understanding the insulating state.

Various theories have been proposed to explain these intriguing experiments. Lee *et al.* [26] have performed LDA+U calculations, which include Na-ordering, but not strong correlations. Other groups [27] have studied strongly correlated models that include the Coulomb interaction with neighbouring sites, but neglect the effects of Na-ordering. Marianetti and Kotliar [28] have also studied the Hamiltonians proposed in [10] for  $x = 0.3$  and 0.7.

In order to compare our results with experiments on  $\text{Na}_{0.5}\text{CoO}_2$  we need to restrict ourselves to the relevant parameter values:  $t < 0$  and  $|t| \sim \Delta \ll U$  [14]. This corresponds with the regime of the three quarters filled ionic Hubbard model that is both the most interesting and the most difficult to study via exact diagonalisation because of the deleterious finite size effects. Nevertheless we propose that in  $\text{Na}_{0.5}\text{CoO}_2$  the insulating state is analogous to a covalent insulator. This explains a wide range of experiments. The peak observed at  $\omega \sim 30$  meV in the optical conductivity [21], is interpreted as the transfer of an electron from the weakly correlated band to form a doublon in the strongly correlated band. The weak charge transfer ( $n_B - n_A = 0.1 - 0.3$ ; c.f., Fig. 1) is caused by the strong hybridisation between the A and B sublattices and is consistent with the value extracted from crystallographic experiments ( $0.12$  [11]) and the bounds from NMR ( $< 0.4$  [22]). The large moment ( $0.1-0.2\mu_B$ ; c.f., Fig. 4) is comparable to the moment found by neutron scattering ( $0.26\mu_B$  [24]) and results from the electrons in the strongly correlated band, i.e., the single spin hybridised between the A and B sublattices. Finite size effects mean that we cannot accurately calculate the charge gap in this

regime. However, we propose that the experimental system corresponds to a parameter range where the gap is small,  $\Delta_c < \mathcal{O}(|t|)$ , consistent with the gap,  $\sim 7\text{-}10$  meV [20, 25], seen experimentally in ARPES and resistivity. This is consistent with the expectation that  $\Delta_c \rightarrow 0$  as  $\Delta/|t| \rightarrow 0$ . Accurately calculating  $\Delta_c$  for small  $\Delta/|t|$  and large  $U$ , and hence further testing our hypothesis, therefore remains an important theoretical challenge.

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- [14] Atomistic calculations give  $t = -(0.08\text{-}0.14)$  eV,  $U = 2.5\text{-}2.8$  eV, and  $\Delta = 0.03\text{-}0.16$  eV [12, 29]. Further,  $\text{CoO}_2$ , which is described by model (1) at half filling with  $\Delta = 0$ , is a strongly correlated metal rather than a Mott insulator [30]. This suggests  $U/|t| \lesssim 12 - 15$ , the critical value for a Mott insulator on the triangular lattice [10, 31].
- [15] The tight-binding band structure of model (1) consists of two bands due to hybridization between *A* and *B*-sites. At 3/4-filling, for  $t > 0$  and any non-zero  $\Delta$ , the lower band is filled and the upper band is half-filled, while for  $t < 0$  the lower band is filled for  $|\Delta| \gtrsim 0.64t$ .
- [16] In the strong coupling limit we find, from degenerate perturbation theory, that, for either sign of  $t$ ,  $n_B - n_A = 1 - 8(t/\Delta)^2 + 16(t/\Delta)^3 + \mathcal{O}((t/\Delta)^4)$ . For  $t = 0$  the ground state of model (1) is a charge ordered insulator consisting of rows of doubly occupied *B*-sites alternating with rows of singly occupied *A*-sites. In the strong coupling limit,  $U \gg \Delta \gg |t|$ , virtual hopping processes lead to magnetic interactions between electrons in *A*-sites. Eq. (1) reduces to a Heisenberg model on an rectangular lattice:  $H = J \sum_{\langle ij \rangle} [\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4}] + J_\perp \sum_{[ij]} [\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4}]$ , where  $J = \frac{4t^2}{U} - \frac{8t^3}{\Delta^2}$  and  $J_\perp = \frac{16t^4}{\Delta^2} [\frac{1}{U} + \frac{1}{2\Delta+U} + \frac{1}{2\Delta}]$ .  $J$  results from the usual superexchange antiferromagnetic coupling and ‘ring’ exchange process around a 3-site plaquette [6]. In our previous paper [10], the  $\mathcal{O}(t^3)$  term was neglected.  $J$  becomes negative for  $t > 0$  and  $\Delta \lesssim \sqrt{2}Ut$  leading to a ferromagnetic interaction. In contrast  $J_\perp$  is always antiferromagnetic.
- [17] The lowest order correction to the charge gap, in the strong-coupling limit, comes from the kinetic energy of a hole (doublon) propagating along the *B*(*A*)-chains when extracting (adding) an electron to the zeroth order ground state configuration. Using degenerate perturbation theory we find that the gap is given, to  $\mathcal{O}(t^3)$ , by  $\Delta_c = \Delta - 2|t| + 4t^2/\Delta - 8t^3/\Delta^2 + E_{1D}^{t-J}$ , where  $E_{1D}^{t-J}$  is the energy of a hole in a half-filled  $t$ - $J$  chain with  $J$  given by the expression in Ref. 16.  $E_{1D}^{t-J}$  is given by the Bethe ansatz expression [32] for  $J > 0$ , while  $E_{1D}^{t-J} = -2|t| - J/2$  for  $J < 0$ .
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